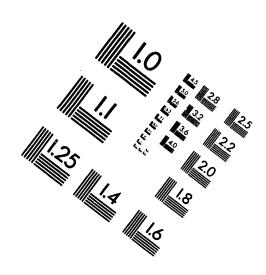
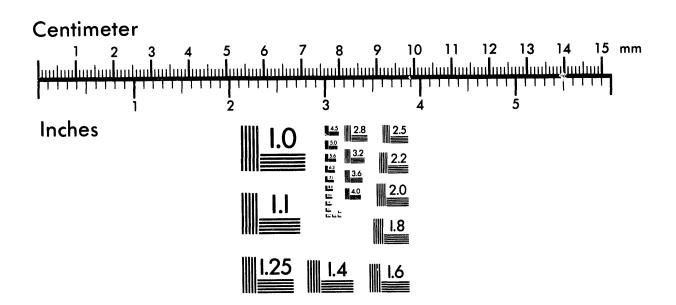


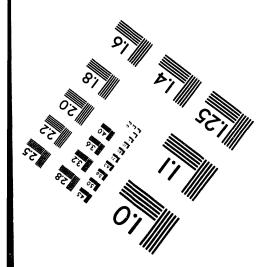


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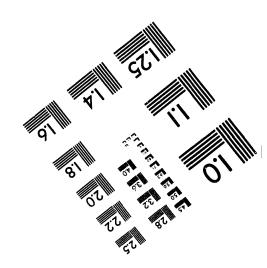




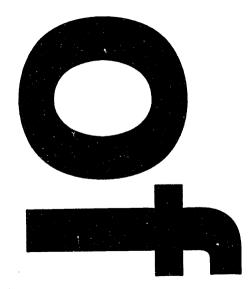


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# IMPROVING RESERVOIR CONFORMANCE USING GELLED POLYMER SYSTEMS

Contract Number DE-AC22-92BC14881

The University of Kansas Center for Research, Inc. Energy Research Center Tertiary Oil Recovery Project

July 8, 1994

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> Reporting Period 3/25/94 - 6/24/94 (7<sup>th</sup> Quarterly Report)

Bartlesville Project Office

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## **Objectives**

The general objectives are to 1) to identify and develop gelled polymer systems which have potential to improve reservoir conformance of fluid displacement processes, 2) to determine the performance of these systems in bulk and in porous media, and 3) to develop methods to predict the capability of these systems to recover oil from petroleum reservoirs.

This work focuses on three types of gel systems - an aqueous polysaccharide (KUSP1) system that gels as a function of pH, the chromium(III)-polyacrylamide system and the aluminum citrate-polyacrylamide system. Laboratory research is directed at the fundamental understanding of the physics and chemistry of the gelation process in bulk form and in porous media. This knowledge will be used to develop conceptual and mathematical models of the gelation process. Mathematical models will then be extended to predict the performance of gelled polymer treatments in oil reservoirs.

# Summary of Technical Progress

Task II: Physical and Chemical Characterization of Gel Systems

### II.2 Examine Chemical Reaction Kinetics

The KUSP1 polysaccharide system gels as the pH of the solution is reduced below a value of approximately 10.8. A method to control the pH reduction of KUSP1 solutions is to use an ester that hydrolyses slowly in the pH range of 10 to 13. Two esters have been identified that meet the requirements of the KUSP1 system. A relatively expensive ester was used in earlier work. A second ester, mono-etnyl phthalate, which is much less expensive was examined this quarter.

A kinetic study of the hydrolysis of mono-ethyl phthalate in the *absence* of KUSP1 polymer was completed. Experiments were conducted in the pH range of 9 to 13 and at 25 °C. Parameters studied were the initial NaOH and ester concentrations. A simple reaction model described the experimental results. The rate equation for the hydrolysis reaction was:

$$\frac{d [A]}{d t} = -k [A] [B]$$

[A] = concentration of ester, mole/liter

[B] = concentration of hydroxide, mole/liter

k = 5.5 liter/mole-second.

Hydroxide concentrations were determined by pH measurements using a calibration curve and ester concentrations were determined by material balance. This model compared well with the experimental data as shown by the results for two formulations in Figure 1.

A kinetic study of the hydrolysis of mono-ethyl phthalate in the *presence* of KUSP1 polymer was initiated. An example of the type of data obtained is given in Task III below.

Study of the polyacrylamide-aluminum citrate system in bulk form continued. Gel systems containing 1200, 900 and 300 ppur polymer and aluminum at polyacrylamide-to-aluminum weight ratios of 20:1 were prepared and gelation monitored by viscometry and the transition pressure. Transition pressure was obtained by a method described in a paper by J.E. Smith (Society of Petroleum Engineers Paper 18739, SPE International Symposium on Oilfield Chemistry, Houston, TX Feb. 8-10, 1989) and is a measure of gel strength. Two important features of this gel system are demonstrated in Figure 2 where the transition pressure as a function of time is shown for two samples containing 300 ppm HiVis 350 polyacrylamide and 15 ppm aluminum. The first feature is shown by Sample A where the transition pressure increased rapidly during the first few hours followed by only a small increase thereafter. These data indicated that the gel structure formed quickly even at the relatively low concentrations of reactants. The second feature is that gelation was affected by the water used to prepare the solutions. Samples A and B were prepared with water purified by two different methods. The transition pressure of Sample B decreased to low values with time as shown in Figure 2. Tests indicated that 0.5 ppm of chlorine in the water used to prepare Sample B caused the degradation of the sample.

### Task III: Mechanisms of In Situ Gelation

It was previously reported that continuous pressure increases in the front sections of Berea sandstone cores were observed during the injection of KUSP1 solutions and that filtration of the polymer solution alleviated the problem. Additional work in which KUSP1 solutions were flowed through Berea core plugs and 5.0 micron filters has shown that an interaction between the polymer and the salt (NaCl) added to the solution produced the injectivity problem.

The KUSP1 polymer system was gelled in a sandpack using the mono-ethyl phthalate ester to trigger gelation. Two pore volumes of a solution containing 2.0 % KUSP1, 0.1 M NaOH and 0.06 M ester were injected within one hour into a foot-long sandpack with an initial permeability of 7000 md. The sandpack was shut-in for 94 hours. Samples of the injected solution and the effluent gelled as shown in Figure 3. The pH of the samples decreased with time as a result of the ester hydrolysis. The pH of the samples decreased to approximately 10.8 which triggered gelation of KUSP1 at approximately 50 to 60 hours as shown by the increase in viscosity in Figure 3. Water was flowed through the sandpack to determine permeabilities 94 hours after the injection of gel solution. The treatment reduced the permeability by a factor of 290 to a value of 24 md. After this initial post-treatment permeability measurement, brine was flowed continuously through the gelled sandpack and permeabilities were determined periodically. The permeability increased to 38 md and has remained at that value.

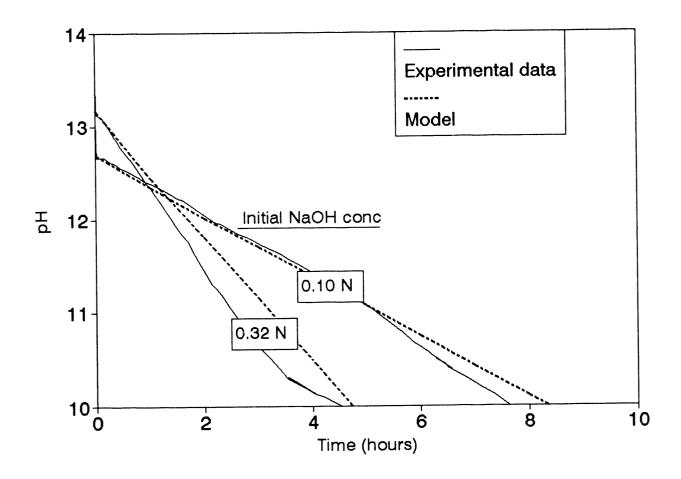


Figure 1: Experimental and Simulated pH Values for the Hydrolysis of Mono-ethyl Phthalate at Two Initial Conditions; NaOH-to-ester mole ratio constant at 1.333.

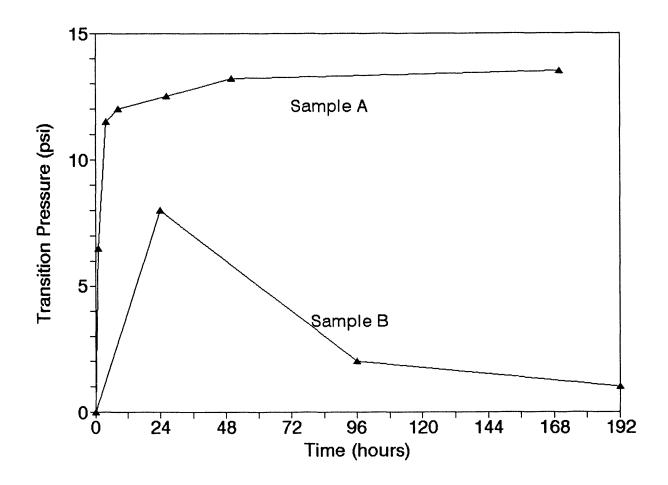


Figure 2: Effect of Water Purity on the Transition Pressure Profiles; 0.0 ppm chlorine in Sample A, 0.5 ppm chlorine in Sample B.

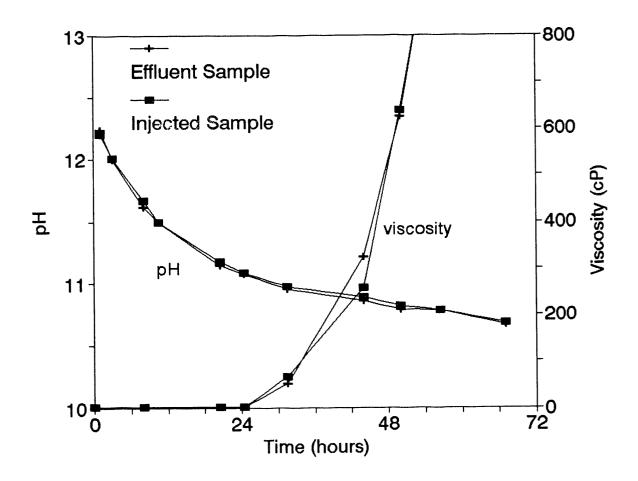


Figure 3: Viscosity and pH Profiles for Injected and Effluent Samples; In Situ Gelation Experiment of KUSP1-Ester Gel System in Sandpack.

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